A STUDY OF THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF LITHIUM CHLORIDE AT 20° C.

BY

WILLIAM HERBERT BAHLKE

A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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ACKNOWLEDGMENT.

The author wishes to express his sincere appreciation of the inspiration and assistance given by Professors Frazer and Lovelace, under whose direction this investigation was carried out.

To them, as well as to Professors Reid, Patrick, Thornton, Bliss, and Pfund, he desires to acknowledge a debt of gratitude for instruction in the lecture room and laboratory.

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THE VAPOR PRESSURE OF LITHIUM CHLORIDE SOLUTIONS AT 20° C.

The method used in measuring the vapor pressure of the aqueous solutions which form the subject of this paper, consist in introducing solutions and solvent in bulbs immersed in the same bath, the temperature of which is accurately regulated, and determining the difference in pressure between the separated systems by means of a Rayleigh manometer. By the method differences in vapor pressure may be measured to within 0.0005 mm. of mercury.

Detailed description of the apparatus may be found in papers by Frazer and Lovelace [1] and Lovelace, Frazer and Miller.[2] No changes in the apparatus were made except that the Gaede pumping system has been replaced by a Langmuir molecular pump, using a three stage rotary oil lamp as auxiliary and fitted with suitably arranged stop-cocks for releasing the pressure. These stop-cocks were in front of trap No. 1 so that no air could leak thru them to the system while measurements were being made.

Purification of Materials.

Efforts to purify the lithium chloride to use in this investigation by means of amyl alcohol were unsuccessful for after distilling six times in an all glass apparatus it still left a residue on evaporation. This method was, therefore, abandoned and the salt prepared from the carbonate.

The original salt was Baker's Lithium Chloride—C. P. The ammonium carbonate used in the precipitation left no residue on sublimation. The preparation is as follows: Lithium chlor-

[1] *J. A. C. S.* (36) 2439 (1914).
[2] *J. Amer. Chem. Soc.* (38) 515 (1916).

ide was dissolved in distilled water and to this solution was added small amounts of a solution of ammonium carbonate, the mixture heated and stirred for four hours, then filtered. In this way any calcium, barium, magnesium, iron or aluminum possibly present were removed. To the filtrate was then added an excess of ammonium carbonate solution and the lithium carbonate filtered off on a Buchner funnel and thoroughly washed with hot water. The carbonate was next heated in a platinum dish at sufficiently high temperatures to volatilize any ammonium chloride possibly present. The salt was then suspended in a small amount of water and pure hydrochloric acid added in small amounts until test portions of the solution reacted neutral to rosolic acid.

Analysis of this solution for lithium and for chlorine checked within 0.04%. This concentrated solution was preserved in a well stoppered bottle and used to make up the more dilute solutions.

Conductivity water was introduced into one of the bulbs in the bath and the solutions were measured against this.

Experimental.

The first requisite in determining the vapor pressure of the solutions is that both solution and solvent be air-free. Tests for air were made by allowing the solution or solvent to come to equilibrium with the vapor over it in a large bulb for twelve hours. The solution was then trapped off and the vapor in the bulb exposed to phosphorus pentoxide for twenty minutes and the residual pressure measured with a McLeod gauge. No solution was considered air-free unless the vapor showed at the end of twenty minutes exposure a residual pressure less than 0.0001 mm. of mercury as measured on the McLeod gauge. The solvent was tested for air just before measuring each pair of solutions.

In former investigations the removal of air has been a time-consuming operation, the solutions requiring from four to six twelve-hour expansions before they could be considered air-

free. In this investigation, however, a method has been devised by which air-free condition may be accomplished in a minimum of time; that is, one twelve-hour expansion.

This is accomplished as follows: The solutions are made up in a flask shaped like the one shown in Fig. 1. The required amount of lithium chloride solution is introduced into the weighed flask by pipetting into the flask a definite number of

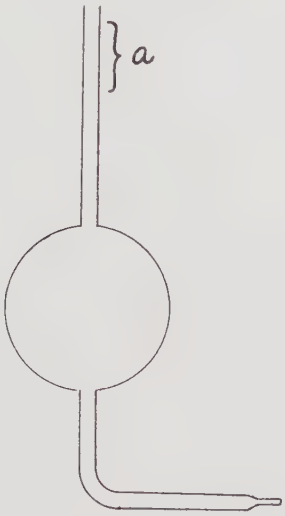


FIGURE 1

cubic centimeters of the mother solution. The required amount of water was next introduced into the flask and the level marked. An excess of water was then added to make up for that lost when the solutions were boiled. The tube was then constricted at the portion " a " and a clean rubber tube was fixed over the end of the glass and fitted with a pinch cock. The lower limb of the flask was heated with a Bunsen flame in order to expel from this portion of the flask as much air as possible. The flame was then applied to the sides of the flask and the solution vigorously boiled for thirty minutes or more until the water level was down nearly to the mark on the flask. The

pinch cock was then closed and the flame removed simultaneously, the solution allowed to cool slightly and the flask sealed off at the constriction. The flask was then weighed with its contents and the weight of the solution noted. Usually about three grams excess water were present, this excess being re-

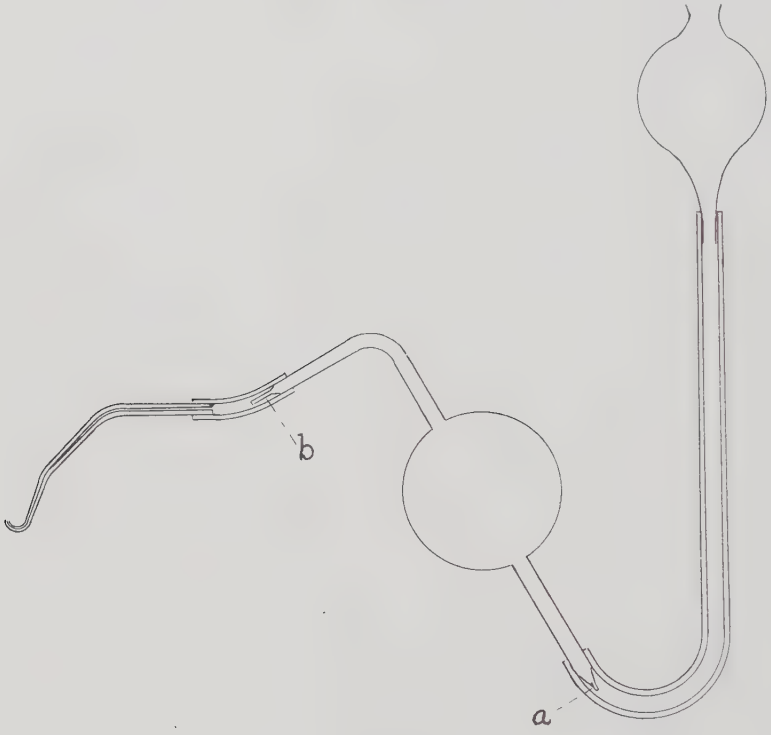


FIGURE 2

moved by a method described below after the solutions were in the bath.

The sealed-up flask was then fixed with a mercury reservoir as shown in Fig. 2, the tube broken at " a " by pressure of the fingers and the mercury allowed to fill the flask completely, the flow being regulated by a pinch cock. Very little leakage of air was experienced in this operation. The tube was then

fitted with a capillary filled with mercury and broken by pressure at "b," some of the solution being wasted to replace the mercury in the capillary. The solution was introduced into the bath by the method described in a former article.[3] In this manner the solutions were introduced nearly air-free.

The bulbs in the bath were previously pumped free from air periodically until on standing no gain in pressure was measured on the McLeod. The time necessary for the removal of air from the walls of the apparatus was shortened somewhat by pulling up the mercury to the bulbs while this part of the apparatus was still wet. In this way a layer of water preceded the mercury up the tubes and tended to sweep them free from air. This water was then removed by exposure to a phosphorus pentoxide bulb. It was found that the time necessary for the removal of air before the introduction of the solutions was considerably shortened.

The solutions after they were in the bath contained usually three grams of water in excess of that required to make them even tenth molar concentrations. This was removed by adjusting the traps so that the solution was exposed to a weighed phosphorus pentoxide bulb for a short period of time (about one minute). The solution was then trapped off and the phosphorus pentoxide bulb weighed and the gain in weight noted. It was found that the gain in weight per unit of time was nearly constant so that in the later solutions the bulb was not weighed but the time of exposure measured. The analysis of the solutions showed that this was sufficiently accurate. It was found that this rapid removal of water from the solutions eliminated the air more rapidly than allowing the solution to come to equilibrium with its vapor, the method previously used.

After trapping off the solution the rest of the apparatus was pumped free from air and the operation just described repeated. The water removed at each operation was sufficiently small so that the procedure might be carried out several times. After

[3] *J. A. C. S.* (42) 1796 (1920).

the proper amount of water had been removed and the expansion bulb pumped free from air the solution was allowed to come to equilibrium with its vapor for twelve hours and the vapor tested with the phosphorus pentoxide and McLeod gauge for residual air. In nearly all cases one twelve-hour expansion was sufficient to remove the air, the whole operation of removal requiring about twenty-four hours. Previously the removal required three to four days and some of the solutions required twenty-five twelve-hour expansions before they could be considered air-free.

Readings.

In making readings of the vapor pressure, lowering the accurate regulation of the temperature described in former articles was followed. Usually three readings of the zero point were made before measuring a solution, three readings of a solution were made, three readings of the second solution made, and then two or more readings of the zero. No readings were regarded as sufficiently accurate unless the zero before and after checked within 0.1 mm. scale deflection.

A set of readings was made by two different observers, extending over two to three days until four reliable sets of readings were obtained on each solution. These readings will be found on pages following.

Readings of the zero are taken by exposing the same system to both sides of the Rayleigh manometer, regulating the height of the mercury column and tilting the manometer until the ground glass points just touch both mercury surfaces. The angle thru which the manometer is rotated when measuring a solution is measured by observing the position of a cross hair in a stationary telescope on a scale reflected by a mirror fixed to the top of the manometer. The lowering is given by the formula:

$$h = \frac{sd}{2D} \cdot \frac{\sin\theta}{\frac{1}{2}\tan 2\theta}$$

where h = lowering.

s = deflection read from scale.

d = distance between points of the manometer.
D = distance from scale to mirror.
θ = angle of rotation of mirror.

Unless the angle θ exceeds one degree the term $\frac{\sin \theta}{\frac{1}{2}\tan 2\theta}$ is sufficiently close to unity to justify the use of the equation

$$h = \frac{sd}{2D} = K \times S$$

This equation has been used to calculate the lowerings at room temperature except in the case of the 1.0 molar solution where the correction for θ has been applied. In the final summary of results the lowerings have been expressed in millimeters of mercury at zero degrees, using 17.539 mm. as the vapor pressure of water at 20°.

Analysis of Solutions.

On removing the solutions from the bath they were put in clean glass stoppered flasks and analysis for chlorine started immediately. The results of these analyses are recorded at the top of the page containing the readings of the corresponding solution.

DATA.

Vapor Pressure Lowerings of Ten Solutions of Lithium Chloride at 20° C.

DATA.

0.09687 M.

Date	*Zero*	*Reading*	*Zero*	*Deflection*
4/30/21	180.9	192.2	181.0	
	181.0	192.1	181.1	
	181.0	192.1		11.10
4/30/21	181.1	192.0	181.1	
	181.1	192.0	181.0	
	181.0	192.0		10.95
5/1/21	181.9	192.9	181.9	
	181.9	192.8	181.9	
	181.8	192.9		10.98
5/1/21	182.0	193.1	182.1	
	182.1	193.1	182.1	
	182.1	193.0		10.98
			Average Deflection	11.00

0.1842 M.

Date	*Zero*	*Reading*	*Zero*	*Deflection*
4/25/21	180.2	201.2	180.1	
	180.2	201.1	180.1	
	180.1	201.1		21.00
4/25/21	180.1	201.0	180.0	
	180.0	201.0	180.1	
		201.2		
		201.0		21.00
4/26/21	180.7	202.1	181.0	
	180.8	202.0	180.9	
	180.9	202.0		21.16
4/26/21	181.9	203.0	181.9	
	182.0	203.1	182.0	
		203.0	182.0	21.11
			Average Deflection	21.07

0.2952 M.

Date	*Zero*	*Reading*	*Zero*	*Deflection*
4/30/21	181.1	215.2	181.1	
	181.1	215.1	181.0	
	181.0	215.1		34.08
4/30/21	180.9	215.1	181.0	
	181.0	215.0	181.1	
	181.0	215.0		34.03
5/1/21	181.9	215.9	181.9	
	181.9	215.8	181.9	
	181.8	215.9	181.9	33.98
5/1/21	182.0	216.1	182.1	
	182.1	216.1	182.1	
	182.1	216.0		33.98
			Average Deflection	34.02

0.3862 M.

Date	*Zero*	*Reading*	*Zero*	*Deflection*
4/25/21	180.2	224.9	180.1	
	180.2	225.1	180.1	
	180.1	225.1		44.90
4/25/21	180.1	225.0	180.0	
	180.0	225.1	180.1	
		225.1		45.01
4/26/21	180.7	225.9	181.0	
	180.8	226.0	180.9	
	180.9	225.9		45.09
4/26/21	181.9	227.2	181.9	
	182.0	227.0	182.0	
		227.0	182.0	45.11
			Average Deflection	45.03

0.4782 M.

Date	*Zero*	*Reading*	*Zero*	*Deflection*
4/18/21	198.1	254.1	198.0	
	198.2	254.3	197.9	
	198.1	254.3		56.19
	197.8	253.9	197.7	
	197.7	254.0	197.8	
	197.8	253.9		56.21
	186.0	242.3	186.0	
	185.9	242.2	186.0	
	186.0	242.2		56.25
	186.0	242.0	185.9	
	186.0	242.2	186.0	
	186.0	242.2		56.16
			Average Deflection	56.20

0.5897 M.

Date	*Zero*	*Reading*	*Zero*	*Deflection*
4/12/21	202.0	272.2	202.2	
	201.9	272.1	202.1	
	202.0	272.3	202.1	70.16
4/12/21	202.0	272.0	201.9	
	202.0	272.1	202.0	
	202.1	272.0		70.04
4/13/21	202.0	272.0	201.9	
	201.8	272.1	201.9	
	202.0	272.0		70.12
4/13/21	202.0	272.0	201.9	
	202.0	272.2	202.0	
	202.0	272.1		70.13
			Average Deflection	70.11

0.7257 M.

Date	*Zero*	*Reading*	*Zero*	*Deflection*
4/6/21	200.0	287.0	199.9	
	200.0	287.1	200.0	
	199.9	287.1		87.11
4/6/21	200.9	287.9	201.0	
	200.9	288.0	201.0	
	200.9	288.0		87.01
4/7/21	201.0	288.0	201.0	
	201.0	288.1	200.9	
	201.0	288.0		87.06
4/7/21	201.0	288.1	201.1	
	201.0	288.1	201.0	
	201.0	288.1		87.07
			Average Deflection	87.06

0.7810 M.

Date	*Zero*	*Reading*	*Zero*	*Deflection*
4/18/21	198.1	292.0	198.0	
	198.2	292.2	197.9	
	198.1	292.0		94.02
4/18/21	197.8	291.8	197.7	
	197.7	291.7	197.8	
	197.8	291.8		94.01
4/20/21	185.9	279.9	185.9	
	185.9	280.0	186.0	
	185.9	280.0		94.04
4/20/21	186.0	280.0	186.0	
	185.9	280.1	186.0	
	186.0	280.0	186.0	94.05
			Average Deflection	94.03

0.9268 M.

Date	*Zero*	*Reading*	*Zero*	*Deflection*
4/6/21	200.0	313.0	199.9	
	200.0	313.0	200.0	
	199.9	313.0		113.05
4/6/21	200.9	314.1	201.0	
	200.9	314.1	201.0	
	200.9	314.0		113.11
4/7/21	201.0	314.0	201.0	
	201.0	314.0	200.9	
	201.0	313.9		112.99
4/7/21	201.0	314.0	201.1	
	201.0	314.1	201.0	
	201.0	314.2		113.07
			Average Deflection	113.05

1.0316 M.

Date	*Zero*	*Reading*	*Zero*	*Deflection*
4/12/21	202.0	329.8	202.0	
	201.9	330.0	202.1	
	202.0	330.0		127.93
4/12/21	202.2	330.0	202.2	
	202.0	330.0	202.0	
	202.0	330.0	202.0	127.94
4/13/21	202.0	330.0	202.2	
	201.9	330.0	202.1	
	202.0	330.0	202.1	127.96
4/13/21	202.0	330.0	201.9	
	202.0	330.0	202.0	
	202.1	330.0		128.01
			Average Deflection	127.96

Room Temp.	M	S	D	$K \times 10^6$	h	$P_o - P$	$\frac{P_o - P}{M}$
25°	0.0968	11.00	3806.8	5109	.05620	.05594	.5779
25°	0.1842	21.07	3806.8	5109	.10764	.10715	.5817
25°	0.2952	34.02	3806.8	5108	.17381	.17303	.5861
25°	0.3862	45.03	3806.8	5109	.23006	.22902	.5930
25°	0.4782	56.20	3806.8	5109	.28712	.28583	.5977
25°	0.5897	70.11	3806.8	5109	.35820	.35659	.6047
25°	0.7257	87.06	3806.8	5109	.44479	.44279	.6101
25°	0.7810	94.03	3806.8	5109	.48040	.47824	.6123
25°	0.9268	113.05	3806.8	5109	.57757	.57497	.6204
25°	1.0316	127.96	3806.8	5094	.65183	.64889	.6290

M = Mols Lithium Chloride per 1,000 grams water.

S = Deflection read from scale.

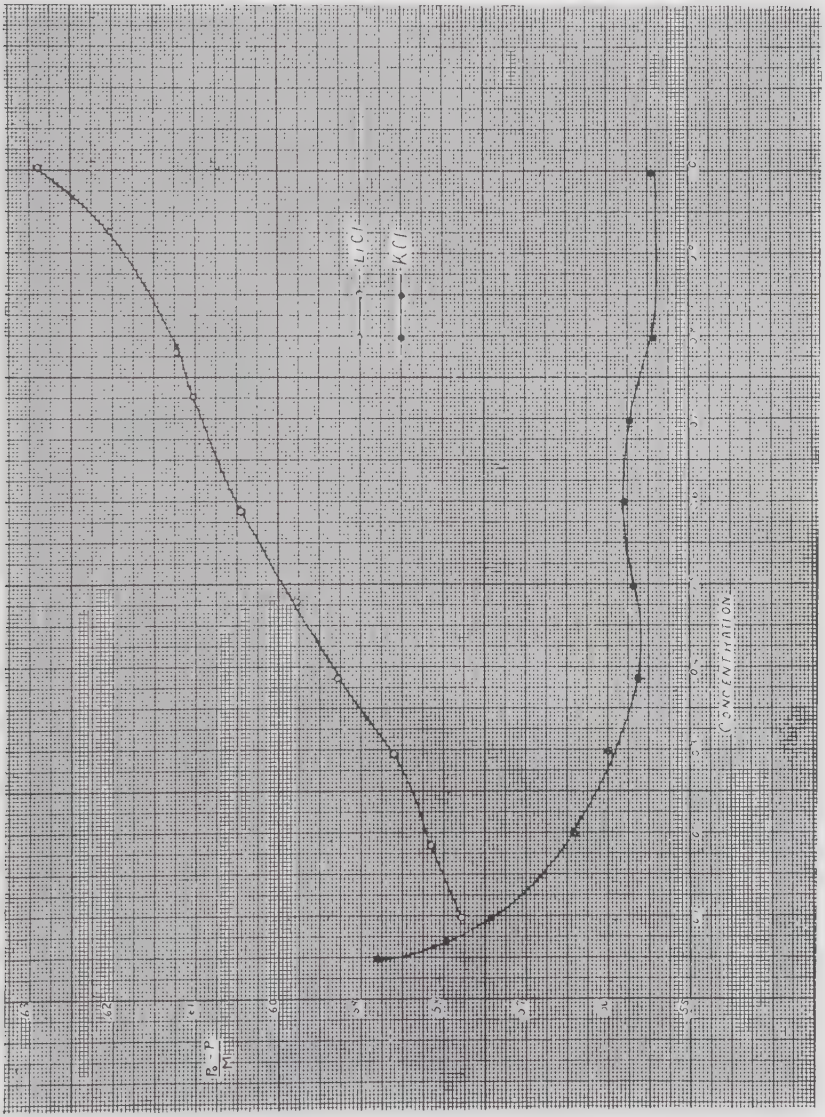
D = Distance from scale to mirror.

d = Distance between points of the Manometer.

$K = \frac{d}{2D} \frac{\sin\theta}{\frac{1}{2}\tan 2\theta}$

h = Lowering of the V. P. as measured.

$P_o - P$ = Lowering corrected to mm. mercury at 0° C.



GRAPH I

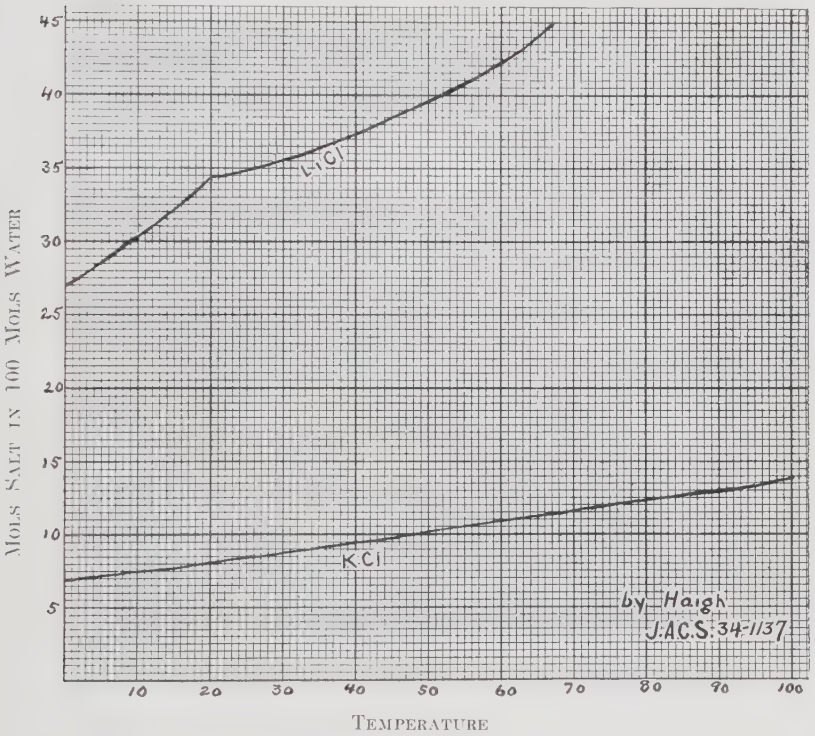
Discussion.

The measurements of the lowering of the vapor pressure of water due to the presence of dissolved substances constitutes one of the most important classes of data for the evolution of a theory of solution. By such means we are able to determine the effect of the concentration of the solute at constant temperature and also with variations of temperature keeping the concentration constant. For this reason it compares favorably with osmotic pressure measurements and with electro-motive force measurements of electrolytes. We would not expect such measurements as freezing point lowering and boiling point rise to yield such reliable data since the temperature at which these measurements are made depend upon the relative amounts of solvent and solute present. Particularly is this true where the solutions possess relatively large heats of dilution, in such cases the temperature at which the measurements are made play a most important part in the conclusions drawn from the results and oftimes the investigator may be led to entirely erroneous ideas concerning the meaning of the data. We must, therefore, admit that our most exact theories must be drawn from the results of osmotic pressure, vapor pressure and electromotive force measurements.

Lithium chloride solutions have been chosen for this investigation because of the anomalies exhibited by such solutions. Also, solutions of potassium chloride have been investigated, using the same apparatus, at the same temperature and thruout the same range of concentrations. Washburn,[4] from freezing point measurements and conductance viscosity data, has found that potassium chloride behaves as a nearly normal solute on the basis of Raoults Law and the vapor pressure measurements of potassium chloride solutions made in this laboratory compare favorably with the calculations of Washburn. However, freezing point measurements of lithium chloride solutions indi-

[4] *J. A. C. S.* (33) 1686 (1911).

cated a marked deviation from Raoults Law, which can be explained only on the assumption that lithium chloride is hydrated in solution. Calculating on the same basis we find that caesium nitrate also shows marked deviations from an ideal solute but the deviation is in the opposite direction; that is, the lowering of the freezing point at higher concentrations is



not great enough for the mol fraction which conductance viscosity measurements indicate. For lack of a better term, then, it is stated that caesium nitrate exhibits "negative hydration" when dissolved in water. We would expect then that vapor pressure lowering due to these uni-univalent electrolytes at temperature other than the freezing point would show also widely different behavior.

Inspection of the solubility curves of lithium chloride and

potassium chloride shown in graph show a distinct break in the lithium chloride curve at 20°. The temperature chosen for this work, then, is just on the point where lithium chloride undergoes a sudden change in solution due to the change of the amount of water associated with each lithium chloride particle. No difficulties occurred in the present investigation due to this change in hydration since the temperature was kept sufficiently constant to overcome this.

Inspection of electromotive force measurements of these two salts show also wide differences in behavior.[5] From these measurements there has been calculated by the authors the activity coefficients of the ions of these two substances. The authors conclude that conductance viscosity ratios do not give us a true idea of the percentage dissociation of electrolytes but that it is better to regard the phenomena of solutions from the standpoint of activity of the ions. The activity coefficient has been defined by Lewis [6] as "that factor which when multiplied by the concentration and substituted in the mass action expression gives a true idea of the equilibrium."

Activity coefficients are readily calculated from electro-motive force measurements.[7] For potassium chloride the various investigators find that there is a steady decrease in the activity with increasing concentration.[8] The results from lithium chloride cells, however, do not agree. Pierce and Mortimer [9] find that the activity coefficients of the ions increase with increasing concentration, while MacInnes and Beattie [10] find that there is first a decrease up to 0.5 molar and then an increase; that is, the curve passes thru a minimum at 0.5 molar. These calculations were made from measurements at 25° and concentrations up to 1.0 molar. It should be remembered here that while e. m. f. measurements give us a direct measure of the

[5] Noyes and MacInnes, *J. A. C. S.* (42) 239 (1920).

[6] *Proc. Am. Acad. Arts Sci.* (43) 239 (1907) and *Zeit. f. phys. Ch.* (61) 129 (1908).

[7] *J. A. C. S.* (42) 242 (1920).

[8] *J. A. C. S.* (42) 243 (1920).

[9] *J. A. C. S.* (40) 509 (1918).

[10] *J. A. C. S.* (42) 1117 (1920).

activity of the solute, vapor pressure measurements depend upon the diminished activity of the solvent molecules due to the solute.

From these considerations then we would expect a wide difference in the curves for the molecular lowerings produced by lithium chloride and potassium chloride. In accordance with the custom, the molecular lowerings for lithium chloride have been plotted against concentration in graph No. 1. On the same graph have been plotted the molecular lowerings of potassium chloride as measured by Lovelace, Frazer and Sease.[11] Inspection of the curves shows a wide difference in the behavior of these two salts in solution. Potassium shows well the effect of dissociation at the lower concentrations while no similar effect is apparent for lithium chloride. The amount of water associated with each particle produced by lithium chloride in solution causes this wide difference in the two curves. Although the amount of water associated with each solute unit decreases with increasing concentration, as is required by the mass action law, the effect of this association increases with increasing concentration for a larger and larger per cent of the solvent will be removed from the sphere of action as the concentration increases which accounts for the upward slope of the molecular lowering curve.

The lowering of the vapor pressure may be calculated from the depression of the freezing point by the following formula given by Washburn.[12]

$$\log \frac{N}{N+n} = \log \frac{P}{P_o} = \frac{\Delta C_p}{R} \log \frac{T_F}{T_o} - \frac{.4343(L_F - \Delta C_P \Delta t_F)}{RT_F} + \frac{.4343LF_o}{RT_{F_o}}$$

where $\frac{N}{N+n}$ = mol fraction of solvent.

P = vapor pressure of the solution.

P_o = vapor pressure of pure solvent.

[11] *J. Amer. Chem. Soc.* (43) 102 (1921).

[12] *Tech. Quarterly* (21) 372 (1908).

T_F = absolute freezing point of the solution.

T_o = absolute freezing point of the solvent = 273 absolute.

L_F = latent heat of fusion of ice = 1435.5 cal.

ΔC_p = difference between mol. heat capacity of ice and water = 9.04 cal.

Δt_F = lowering of freezing point in degrees.

R = gas constant = 1.985 calories.

Using this formula, the vapor pressure lowerings have been calculated from the freezing point measurements given by Washburn,[13] and the results are found in the following table:

Mols. L. Cl per 1000 g. water	Δt_F	Log $\frac{P}{P_o}$ (F.P.)	$P_o - P$ F.P.	$P_o - P$ 20°	Difference Calc. obs.
0.1	0.351	—0.00133	0.054	0.056	—.002
0.2	0.694	—0.00284	0.115	0.117	—.002
0.3	1.049	—0.00442	0.178	0.175	.003
0.4	1.416	—0.00596	0.239	0.236	.003
0.5	1.791	—0.00752	0.311	0.300	.011
0.6	2.174	—0.00913	0.365	0.365	.000
0.8	2.966	—0.01253	0.499	0.485	.014
1.0	3.792	—0.01595	0.633	0.648	—.015

Inspection of the table will show that the agreement is not so close as that for potassium chloride, and that in most cases the difference between the calculated and the observed values is positive. This is to be expected since lithium chloride solutions possess relatively large positive heats of dilution, a large portion of which may be due to combination with the water. Log $\frac{P}{P_o}$ should not remain constant therefore for constant concentration and varying temperature but should decrease with increasing temperature.

[13] *J. A. C. S.* (33) 1701 (1911).

Summary.

The vapor pressure of Lithium Chloride solutions has been measured at 20° C. in the concentration range 0.1 Molar to 1.0 Molar.

An improved method of removing the air from the solutions before measuring has been devised.

The measured pressure have been compared with those calculated from freezing point measurements.

BIOGRAPHY.

The author was born at Baltimore, Maryland, November 7th, 1895. His early education was received in the Public Schools at Richmond, Virginia. He entered Richmond College in 1912 and was graduated with the degree of Bachelor of Science in June, 1916. In October of the same year he entered the Johns Hopkins University as a graduate student in Chemistry. Physical Chemistry and Physics were his subordinate subjects. During the period from June, 1917, to March, 1919, he was on active duty with the National Naval Volunteers. During the years 1917-18 and 1919-20 he held a Hopkins Scholarship and for the year 1920-21 he held a DuPont Fellowship.